THIS IS UNEVALUATED INFORMATION

MECHANISM OF THE NITRATION OF PARAFFINS AND CYCLOPARAFFINS WITH NITROGEN PENTOXIDE

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The reaction between nitrogen pentoxide and paraffins or cycloparaffins is outstanding in the field of saturated hydrocarbon chemistry in that it proceeds smoothly under ordinary conditions without participation of external factors. The high activity of nitrogen pentoxide towards paraffins was first noticed by N. Ya. Dem'yanov [1] over 50 years ago in the reaction with diisoamyl. From the products of the reaction, he separated a small quantity of a primary nitrocompound. After studying the nitroproduct, Dem'yanov was inclined to accept the formula $C_9H_{19}NO_2$ for it, assuming that the carbon skeleton broke down during the reaction. Apparently unaware of Dem'yanov's work, Adkins and Haines [2] discovered a rapid reaction between n-heptane and nitrogen pentoxide 25 years later but were unable to isolate any definite product. Undoubtedly, the inconclusive results of this work prevented other researchers from continuing the study of this unusual reaction.

In our investigations, it was first shown that the reaction between nitrogen pentoxide and the paraffin chain can be successfully accomplished in inert solvents at temperatures below 0°. Under these conditions, the principal products of the reaction were alkyl nitrates (60-65%), nitroalkanes (10-15%), and carboxylic acids (10-15%). In the reaction with cyclohexances, the almost exclusive products of the reaction were cyclohexyl nitrite, nitrocyclohexane, and adipic acid, while in the reaction with n-heptane or octane, secondary alkyl nitrates and nitrocompounds with the predominance of disubstituted isomers in the mixture were formed.

In accordance with the theory of nitration of paraffin chains developed by us [3], the first stage of the reaction must be the formation of a free alkyl group resulting from the action of a suitable radical agent on the hydrocarbon, which is capable of removing hydrogen as follows:

$$R - H + A \cdot = R \cdot + HA. \tag{1}$$

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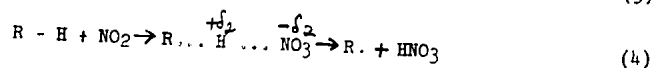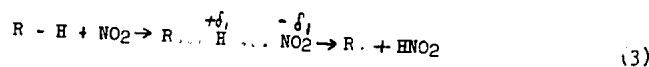| STATE	X	NAVY	X	NSRB		DISTRIBUTION						
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As a rule, in other cases of nitration, the monomeric molecule of nitrogen dioxide serves as such an agent. However, as evidenced by the great rate of the process, nitration with nitrogen peroxide involves the action of a more highly active agent. We assumed that in the reaction of paraffins with nitrogen pentoxide, the NO_3 group serves as such an agent. It is formed in the equilibrium dissociation

$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \tag{2}$$

similarly to that taking place in the cases of N_2O_3 and N_2O_4. The greater activity of NO_3, as compared with NO_2, is due to the stronger electrophilic character of the trioxide. In the first approximation, the electrophilic properties of NO_3 and NO_2 are related to each other as the strengths of nitric and nitrous acids $HONO_2$ and $HONO$. In the corresponding intermediate stages of elementary reactions (3) and (4):

$$R - H + NO_2 \rightarrow R \overset{+\delta_1}{\ldots} H \ldots \overset{-\delta_1}{NO_2} \rightarrow R \cdot + HNO_2 \tag{3}$$

$$R - H + NO_2 \rightarrow R \ldots \overset{+\delta_2}{H} \ldots \overset{-\delta_2}{NO_3} \rightarrow R \cdot + HNO_3 \tag{4}$$

$\delta_2 > \delta_1$, hence a lowering of 15-20 kcal in activation energy takes place. In agreement with our hypothesis, further transformations of alkyls must take place in the same way as nitration through a preliminary interaction of the paraffin with a monomer of nitrogen dioxide NO_2.

The proposed mechanism of the reaction of paraffins with nitrogen pentoxide was verified by many observations. The most important of these was the discovery of a clearly defined inhibiting action of nitrogen dioxide on the rate of the reaction of nitrogen pentoxide with the paraffinic chain -- an effect which is diametrically opposed to the action of nitrogen dioxide in nitration with nitric acid of moderate concentrations. The retarding action of the dioxide was brought about by a decrease in the concentration of NO_3, owing to a shift of the equilibrium in equation (2) to the side of N_2O_5 formation, analogous to that which we observed in the saturation of a mixture of oxides of nitrogen and hydrocarbons with nitric oxide

$$N_2O_3 \rightleftharpoons NO_2 + NO. \tag{5}$$

When the quantities of N_2O_3 and N_2O_4 were equal, the rate of the reaction was reduced several times.

Investigation of the kinetics of the reaction showed that it proceeds approximately according to a bimolecular type, and in accordance with theory, its rate increases in the region of low concentrations of N_2O_5. For N_2O_5, a dependence analogous to the well-known effect of the increase of the degree of dissociation of N_2O_4, when it is transferred from a solution in hydrocarbon to a solution in carbon tetrachloride, may be expected. This conclusion was indirectly confirmed by a significant increase in the rate /of reaction/ in CCl_4 as compared to its rate in octane.
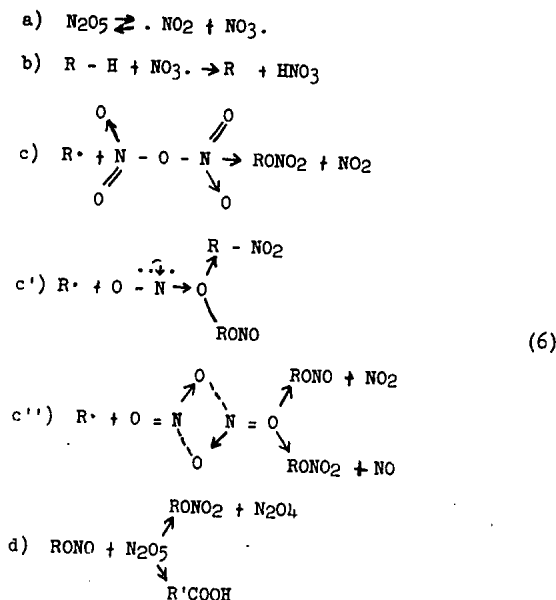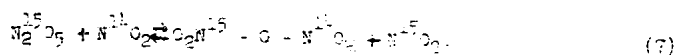
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In accordance with theory, the most probable transformations of the radicals under the conditions of nitration with nitrogen pentoxide may be expressed by the following scheme:

a) $N_2O_5 \rightleftarrows NO_2 + NO_3$.

b) $R - H + NO_3 \rightarrow R + HNO_3$

c) $R\cdot + N\text{(-O-)}N \rightarrow RONO_2 + NO_2$

c') $R\cdot + O - N \rightarrow O \nearrow R - NO_2 \searrow RONO$

c'') $R\cdot + O = N \cdots N = O \rightarrow$ RONO + NO_2 / RONO_2 + NO

d) RONO + N_2O_5 $\nearrow$ RONO_2 + N_2O_4 $\searrow$ R'COOH

(6)

The relation between the observed yields of nitrocompounds and oxidation products must depend on the magnitude of $\dfrac{[NO_2]}{[N_2O_5] + [N_2O_4]}$ and the effectiveness of the corresponding components.

In conformity with this conclusion, we found that when the reaction takes place at elevated temperatures and a constant pressure of N_2O_5, i.e., under conditions that are favorable for the interaction of the radicals with NO_2, the yield of nitroalkanes is increased. Carrying out the reaction in boiling CCl_4 resulted, in the case of nitration of cyclohexane with nitrogen pentoxide, in practically equal amounts of the nitroproduct (39%) and cycloalkyl nitrate (41%), similar to what was observed in the nitration with NO_2 under these conditions. By means of a control experiment, it was established that under the conditions of the reaction with N_2O_5, the role of NO_2 as a radical-forming agent can be disregarded.

As we concluded our work, Ogg's papers /4_7 became known to us. In them, he establishes the rapid formation of the equilibrium $N_2O_5 \rightleftarrows NO_2 + NO_3$ by studying the rate of isotope exchange in the reaction

$$N_2^{15}O_5 + N^{14}O_2 \rightleftarrows O_2N^{15} - O - N^{14}O_2 + N^{15}O_2.$$ (7)

These data represent a full proof of the correctness of our interpretation of the mechanism of nitration with N_2O_5.
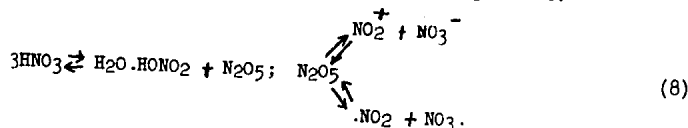
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The results of our research now allow us to explain rigidly the part played by nitrogen pentoxide and nitrogen trioxide in a number of cases of nitrations and to confirm our earlier assumption that these oxides participate in the nitrations. For example, the capacity of highly concentrated or anhydrous nitric acid to react with paraffins under ordinary conditions, as observed by Markovnikov $\underline{/5\_7}$ and other authors, can be definitely explained by the presence of trioxide of nitrogen in such an acid, arising by the following scheme:

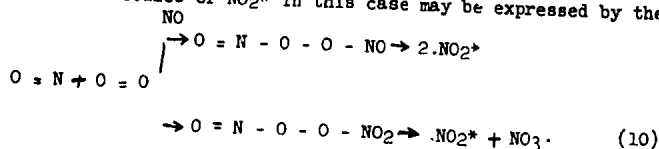$$3HNO_3 \rightleftarrows H_2O.HONO_2 + N_2O_5; \quad N_2O_5 \quad \begin{array}{c} \nearrow NO_2^+ + NO_3^- \\ \\ \searrow .NO_2 + NO_3. \end{array} \tag{8}$$

The formation of N_2O_5 in anhydrous HNO_3 follows from a series of data.

At high-temperature nitration with nitric acid in the gas phase, the formation of active NO_3 is due to the following sequence of rapid reactions:

$$2HNO_3 \rightarrow N_2O_5 + H_2O; \quad N_2O_5 \rightarrow N_2O + NO_3 \quad \underline{/N_2O_5 \rightarrow NO_2 + NO_3?\_7}. \tag{9}$$
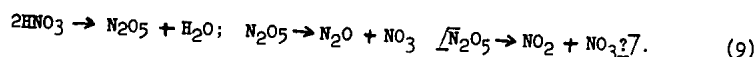
In these circumstances, nitration with nitric acid under the conditions in question can sometimes take place faster than the reaction with nitrogen dioxide. Nitric oxide, rapidly eliminating NO_3, must, under these conditions, have a retarding effect on the reaction.

In our experiments on nitration in the presence of oxygen in the liquid phase $\underline{/3\_7}$, and in the experiments of Has. $\underline{/6\_7}$ in the vapor phase the process of oxidation of nitric oxide with oxygen must have brought about the formation of NO_3 and, consequently, an acceleration of the nitration. The formation of active NO_3 and activated molecules of NO_2^* in this case may be expressed by the scheme

$$O = N + O = O \quad \begin{array}{l} \nearrow NO \\ \rightarrow O = N - O - O - NO \rightarrow 2.NO_2^* \\ \\ \rightarrow O = N - O - O - NO_2 \rightarrow .NO_2^* + NO_3. \end{array} \tag{10}$$

We shall describe some of the experiments as follows:

1. A mixture of 21.6 g N_2O_5, 100 ml CCl_4, and 8.4 g cyclohexane was left standing over night at 0°. Then, 1.2 g of adipic acid were isolated from a bicarbonate extract. From the neutral residue, 1.2 g nitrocyclohexane and 6.5 g cyclohexyl nitrate with a boiling point of $95^\circ - 96^\circ$ at 40 mm, $d_4^{20} = 1.035$, $n_D^{20} = 1.4578$, MR = 36.60 (calculated 35.71) were obtained by vacuum distillation and treatment with alkali; N found 9.26%, calculated 9.62%. Cyclohexyl nitrate was also synthesized by treating cyclohexylnitrite with N_2O_5 (bp $95^\circ - 96^\circ$ at 40 mm, $d_4^{20} = 1.090$, $n_D^{20} = 1.4575$) and esterification of cyclohexanol with N_2O_5 ($d_4^{20} = 1.082$, $n_D^{20} = 1.4575$). The cyclohexyl nitrate from the reaction product was transformed by reduction with zinc in acetic acid to cyclohexyl acetate. Saponification of the latter with 20% KOH resulted in cyclohexanol with a boiling point of $158^\circ - 160^\circ$.

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2. Carrying the reaction out in boiling CCl_4 by adding 32.4 g N_2O_5 over a period of 30 min gave 2.62 g of adipic acid, 8.0 g nitrocyclohexane, and 9.5 g cyclohexyl nitrate.

3. Nitration with a mixture of phosphoric anhydride and anhydrous nitric acid gave results analogous to 1 and 2.

4. Nitration of n-heptane under the conditions of Experiment 1 produced around 1.9 g sec-nitroheptane (d_4^{20} = 0.931, n_D^{20} = 1.4220, MR = 42.20; N found 8.42%, calculated 8.70%). Heptyl alcohol (bp 158° - 161°) was obtained from heptyl nitrate over heptyl acetate. From this was prepared the semicarbazone of heptanone with a melting point of 115° - 120° and 122° - 124° after recrystallization (according to the literature, the semicarbazone of methyl-n-amyl-ketone melts at 124°).

5. Nitration of n-octane under the conditions of Experiment 1 yielded about 1.70 g sec-octane and 9.0 g n-octyl nitrate with a boiling point of 109°-110° at 40 mm (d_4^{20} = 0.9548, n_D^{20} = 1.4260; N found 7.78% calculated 8.00%). Carrying out the reaction in boiling CCl_4 gave results analogous to those of Experiment 2.

Octyl nitrate was similarly transformed into octyl acetate with a boiling point of 185° - 190° (according to the literature, the acetate of octanol-2 boils at 189° - 193°), then into octanol with a boiling point of 175° - 177° (according to the literature, octanol-2 boils at 177° - 179°), and finally into a semicarbazone with a melting point of 116° - 118° and 2,4-dinitrophenyl-carbazone of octanone melting at 48° - 50°, and after recrystallization, at 120° and 56° - 57°, respectively. A noticeable drop in the melting point of mixtures of the products with substances of known structure was not noticed.

Nitro-octane was also transformed into octanone, according to S. S. Nametkin. Investigation of his dinitrophenylhydrazone showed that sec-nitrooctane also consists basically of a two-substituted product.

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